Influence of Atmospheric Weathering on the Performance of Whetlerite

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Commercial samples of ASC whetlerite, Lot 2-281, were exposed to specified flows of untreated outdoor air at the Naval Research Laboratory, the Atmospheric Physics facilities of the Argonne National Laboratory, and the Simi Valley Monitoring Station of the Air Pollution Control District of Ventura, California. The exposures were varied from one to 12 months. The air contaminants and moisture parameters were determined.

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20. ABSTRACT (Continued)

After the exposures, the whetlerite samples were evaluated by CK (cyanogen chloride) tests, by DMMP (dimethyl methyl phosphonate) tests, and for a limited number by AC (hydrogen cyanide) tests. An analysis of the meterological and industrial environments on the performance of the whetlerite will be presented.

The CK "life" of whetlerite is essentially destroyed as the result of the exposure to outdoor air during the hot and humid summer months or in warm climates. Whetlerite is relatively stable in outdoor air flows during cool, dry winter months. The results for DMMP life were found to be location dependent. A good correlation was found between the loss of CK activity and the dew point of the air flow.

CONTENTS

FOREWORD

ASC whetlerite, an impregnated activated carbon, is currently a standard adsorbent choice for military filters. The early versions of whetlerite introduced in World War I used various impregnations, but it was not until 1942 that the special mixture of copper, silver, and chromium was recognized. The copper-impregnated charcoal was called whetlerite A (after J.C. Whetzel and E.W. Fuller) and this has been replaced by the ASC grade.

The term "weathering" is one of three experimental procedures which result in reduced performance of whetlerite. First, "aging", which connotes shelf life, refers to storage in closed containers. Second, "service-aged" whetlerite indicates an exposure to an air flow containing the toxic gas of interest. Third, "weathering" signifies an exposure to either the contaminants of outdoor air or an exposure to a laboratory controlled concentration of the atmospheric contaminants.

Investigations on whetlerite have been dominated previous to this study by a need to qualify new material. Since whetlerite must be ready at any period in its service to play its role in the elimination of the specified toxic gas, the objective of this study has been directed to its performance during long-time service.

INFLUENCE OF ATMOSPHERIC WEATHERING ON THE PERFORMANCE OF WHETLERITE

1. INTRODUCTION

The qualification tests for whetlerite have been established for a number of years for newly produced material. However, a large question remains as to the performance of the impregnated charcoal in long-time service. In actual practice, whetlerite is exposed, either continuously or intermittently, to air flows containing many local contaminants and it is not known to what extent these factors may influence the efficiency of whetlerite.

A sizable quantity of contaminants may enter a carbon bed during service. An annual flow of air of 84×10^6 cubic feet (40 FPM through a bed 2 ft x 2 ft x 3 in) containing 1 ppm of a single pollutant is not a heavy load through the cubic foot of charcoal. However, there are many pollutants. The major species known to react with charcoals are sulfur dioxide, nitrogen oxides, and oxidants such as ozone. Other species known to be present in the air flow are the hydrocarbons, carbon monoxide and carbon dioxide. An estimate of contaminants entering a 30,000 cfm carbon filter in 90 days is given in Table 1. The inlet concentrations of carbon monoxide and carbon dioxide are high, but very little is retained by the charcoal. The retention of hydrocarbons is obviously selective with species, for example very little methane is retained but almost all high molecular weight vapors are retained.

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TABLE 1. CONTAMINANTS ENTERING A 30,000 CFM FILTER CONTAINING 3750 LBS CHARCOAL

	PPM (V/V) (3-yr avg at NRL)	Weight in 90 Days (lbs)	Wt. % of Charcoal
Ozone	0.019	10	0.27
SO_2	0.023	16	0.43
NO_2	0.043	21	0.56
CO	1.37	416	11.0
Hydrocarbons (Non-CH_4)	0.23	214 (Hexane)	5.0

An additional and significant parameter is water vapor. High humidities may accelerate the interaction of hydrated pollutants with the charcoal and lead to a more rapid degradation of the removal efficiency. It is known, for example, that prolonged exposures of nuclear carbons (KI_x-impregnated charcoals) to 90-95% RH air flows result in degradation of methyl iodide trapping; the extent to which this behavior is aggravated in the presence of air pollutants has also been studied (1).

The records (2) of the National Weather Station (National Airport) were examined over 12-month periods (Figure 1.) The dew points varied from 10 to 70°F and the partial pressure of water vapor from 5 to 30 torr. The corresponding mass of water vapor in the air varied from 4 to 40 grams/cubic meter. The flux of water into and out of charcoal is dependent on the relative humidity. The long duration of the exposure to air of a high dew point raises concern for possible chemical degradation of whetlerite.

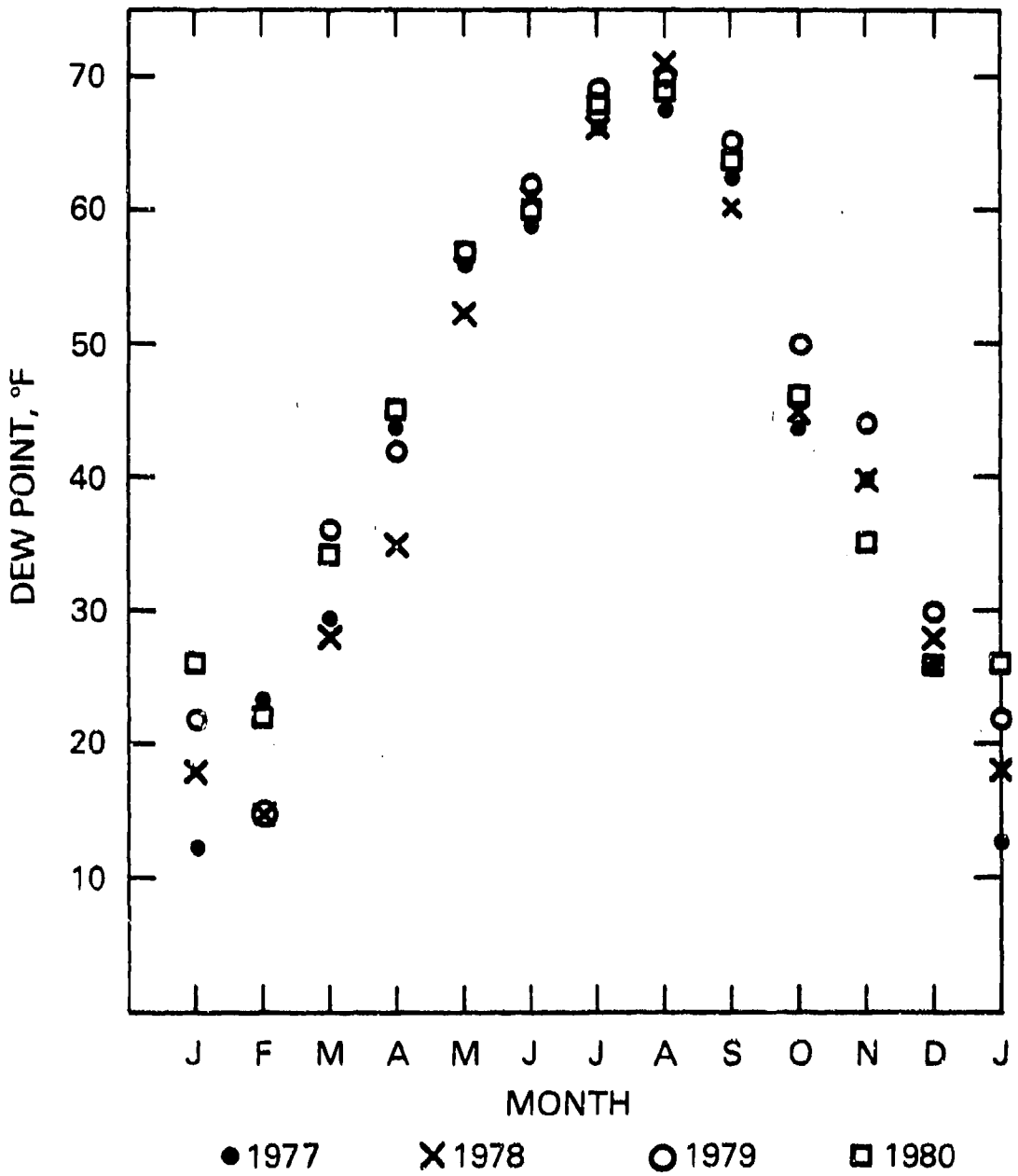

Figure 1. Monthly Average of Dew Points Observed at the National Airport (1977, 1978, 1979, 1980)

It is evident that a record of the air pollutants passing through whetlerite and a knowledge of the exposure to water vapor, followed by systematic CK testing of the samples, will further an understanding of the vulnerability of whetlerite efficiency over long exposures to ambient air.

The surface composition of whetlerite is quite complex and is subject to change. The ASC impregnating solution contains basic copper carbonate, aqueous ammonia, ammonium carbonate, chromic anhydride, silver nitrate, and water. A slurry mode of this solution and the charcoal is drained and the mixture heated in a rotary dryer to a maximum temperature of 180°C. The exact forms that the impregnants then take are not known. Some components may be adsorbed by the charcoal, a part may form a finely divided powder in intimate contact with the surface. For example, the adsorption of chromate chromium from the ACS solution is very slow and is accompanied by some reduction to the trivalent state. In a 30-minute contact of the impregnation, only 0.1% of the chromium may be adsorbed. Consequently, the subsequent aging process in the presence of water vapor may continue the adsorption process, as well as influence other changes. Whetlerite is buffered by the ammonium carbonate system and the acidic air contaminants may react chemically, thus reducing the buffering capacity. The "bottom line" in judging the extent of weathering is the determination of the CK life and this means has been followed in this study.

2. PRELIMINARY WEATHERING EXPERIMENTS IN 1977

ASC whetlerite, Lot 2-291, was exposed to flows of unmodified outdoor air at NRL in a stainless steel container (Figure 2). The diameter of the bed was 4 inches, and the height 2 inches; each bed was divided into four equal layers, each 0.5 inch, by perforated stainless screens. After the exposure, the whetlerite withdrawn from each layer was forwarded to the Army's Chemical Systems Laboratory for evaluation of the weathered samples. By this procedure the vertical gradient of the contaminants through the complete bed could be observed by the testing of the charcoal in each layer.

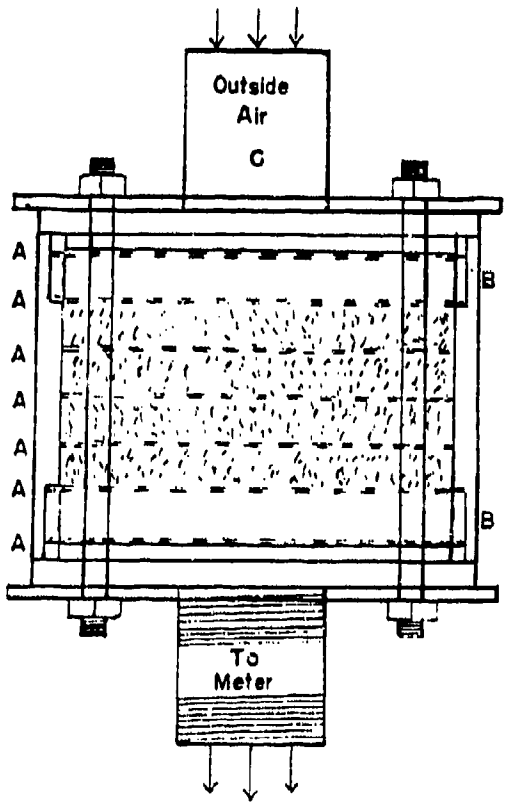

Figure 2. Container (Stainless) for Test Carbon with Perforated Stainless Steel Separators (A) with Spacer Rings (B) at Entrance and Exit and Inlet and Outlet Tubes (C) 1-3/8 in. I.D.

The duration of the preliminary exposures varied fourfold and the volume of air about fivefold (Table 2). The weather during these exposures covered the months May to February, and detailed meterological records were obtained from the Local Climatological Data. The station at the National Airport is close to NRL (2 miles).

TABLE 2. EXPOSURE PARAMETERS IN WEATHERING WHETLERITE (1977)

	Date ON	Date OFF	Duration, days	Air, M^3	Linear velocity, M/min	Weight inc. %
5011	3 May	26 May	23	1270	8.53	11
5018	2 Jun	30 Jun	28	2720	8.53	20
5026	14 Jul	22 Aug	39	4680	8.84	27
5041	11 Sept	3 Nov	53	7742	10.36	27
5062	16 Nov	4 Feb 78	80	10307	10.97	6

The results (Table 3) are given as the time (minutes) to CK breakthrough as a function of dry weight of sample. A control of new whetlerite was run in each evaluation and the CK life relative to new material was calculated. The results on this basis are presented in Table 3 for two weights of whetlerite, 5g and 6g, and for each layer of the five weathered samples.

TABLE 3. THE CK LIFE RELATIVE TO NEW WHETLERITE

$$\text{Relative CK life} = \frac{\text{time of each layer}}{\text{time of control}}$$

Layer	5011	5018	5026	5041	5062
	weight = 5g				
1 (inlet)	0.31	0.30	0.13	0.23	0.22
2	0.36		0.28	0.45	0.61
3	0.39		0.32	0.54	0.67
4	0.41	0.51	0.29	0.55	0.72
	weight = 6 g				
1 (inlet)	0.36	0.37	0.20	0.22	0.21
2	0.42		0.32	0.46	0.53
3	0.46		0.34	0.52	0.62
4	0.50	0.54	0.38	0.54	0.58

Some conclusions may be drawn from these few early results. First, there is a definite degradation of whetlerite over exposure periods up to 80 days. This is a relatively short period compared to actual exposure times and does raise a question as to the efficiency of a whetlerite filter after long service.

Second, the entrance layer of the weathered whetlerite attained the least efficiency. The pronounced profile through the two-inch bed demonstrated a "guard bed" behavior of the entrance layer (0.5 inch). It was thought to be of interest to deepen the bed and explore whether additional whetlerite yields more protection in weathering. Since the results in Table 3 indicate about the same profile of efficiency through 5g samples

as through 6g samples, therefore, it is not clear how the weathering of additional whetlerite would help the efficiency of a filter over the long exposure times in practice.

There appears to be some correlation of weathering with the average dew point during an exposure. Although the duration lengthened in the last three tests of Table 2, the efficiency of the 4th layer increased.

	time(days)	Life, 4th layer	dew point, °F
5026	39	.38	60
5041	53	.54	40
5062	81	.58	28

Decreasing dew point temperatures indicate less moisture in the air to take part in the chemical reactions of degradation. The influence of absolute humidity in degrading whetlerite is a problem worthy of more study.

The graphs of Figures 3, 4, 5, and 6 show the considerable average variation of temperature and dew point during the four tests 5011, 5018, 5026, and 5041. There is also an hourly variation, as shown for relative humidity in Figure 7. During the continuous flow of air, it is possible to add to or subtract from the moisture in a whetlerite and the final few days of exposure may control the observed weight change relative to the initial dry weight of the sample. The weight changes are given in Table 4. The exposure 5011 shows a distinct gradient in moisture content among the four layers that corresponds (see Figure 7) to the drying of the whetlerite as the relative humidity decreased.

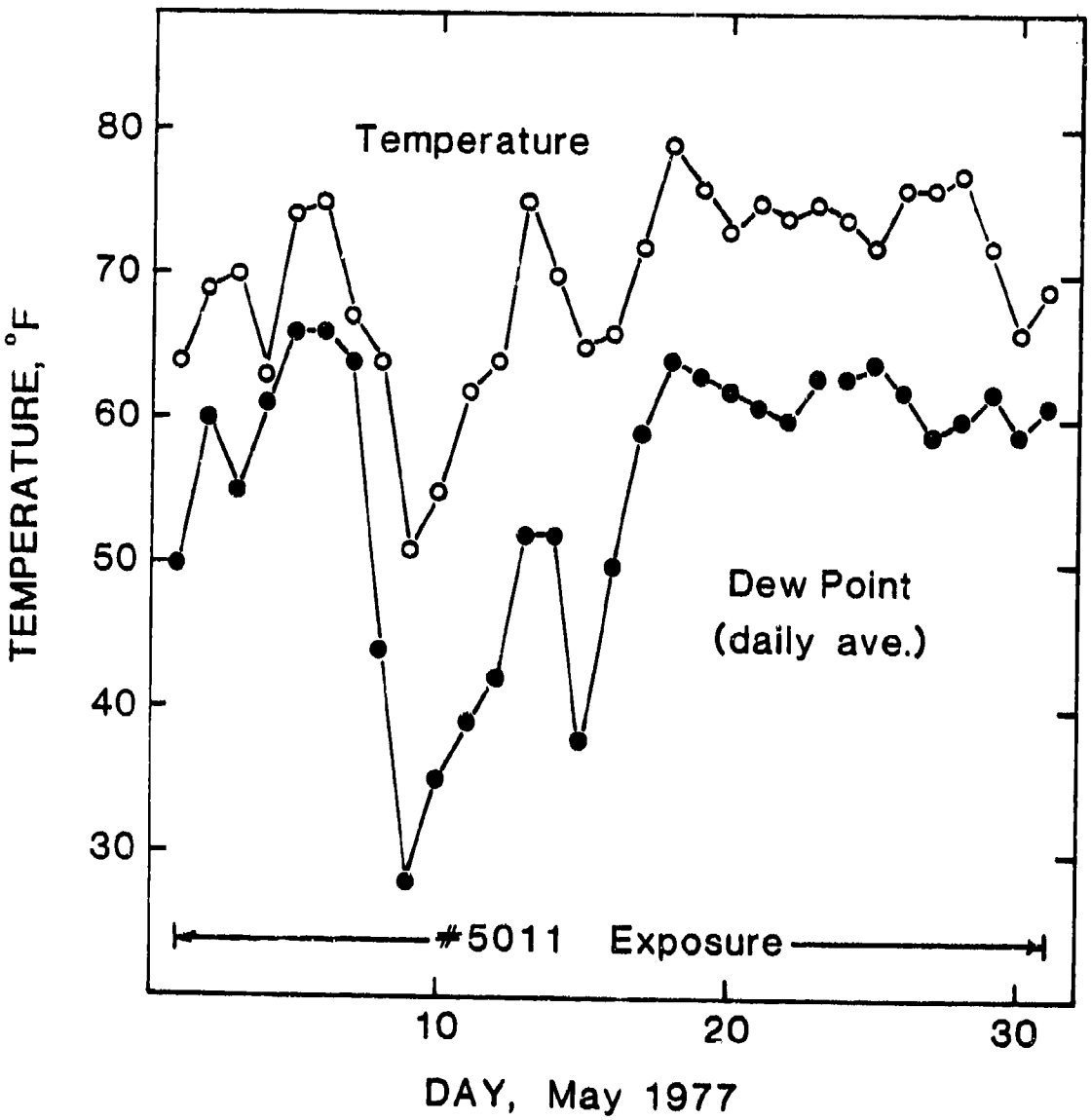

Figure 3. Variations of the Average Daily Temperature and Dew Point During Exposure 5011 at NRL

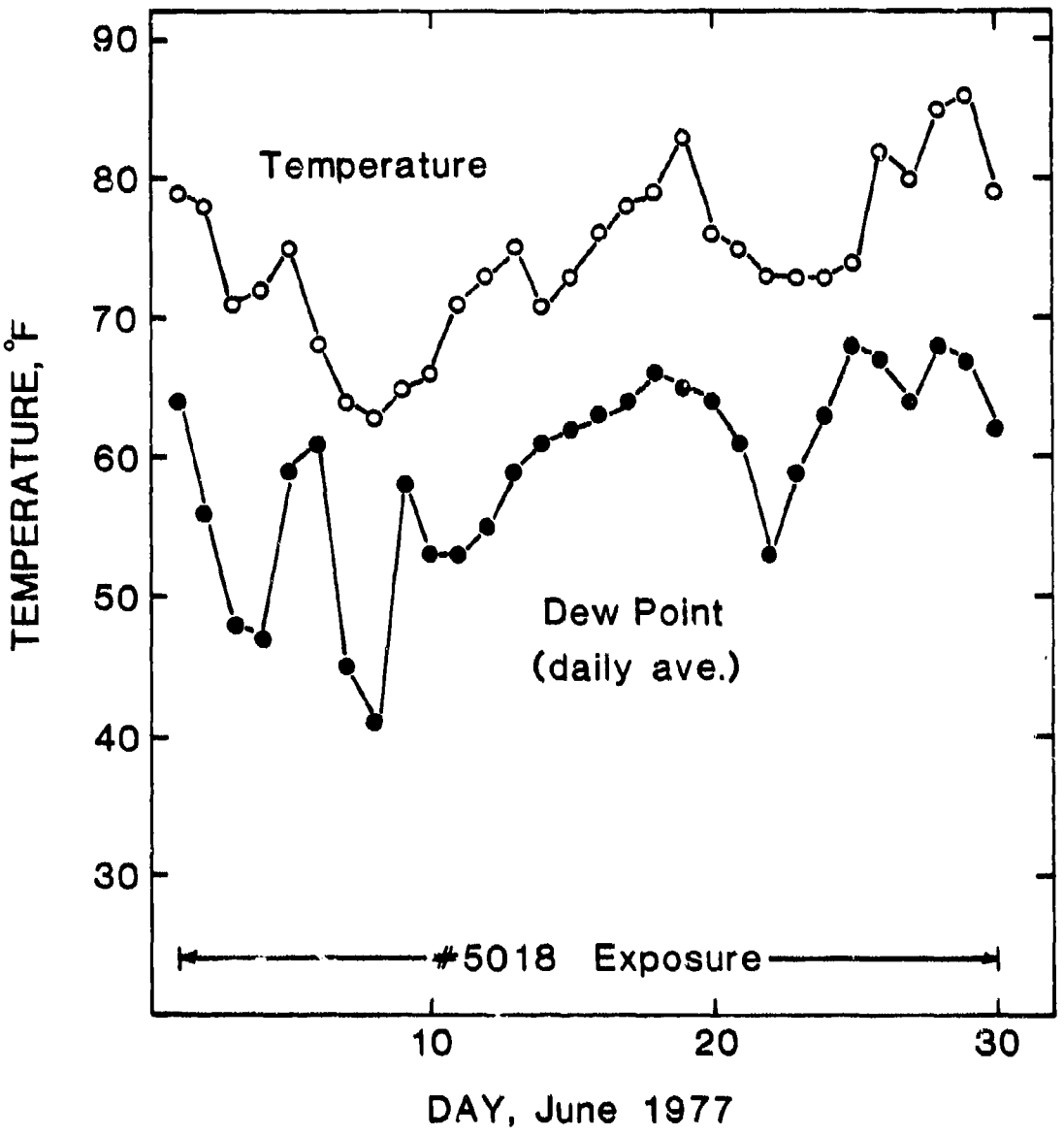

Figure 4. Variations of the Average Daily Temperature and Dew Point During Exposure 5018 at NRL

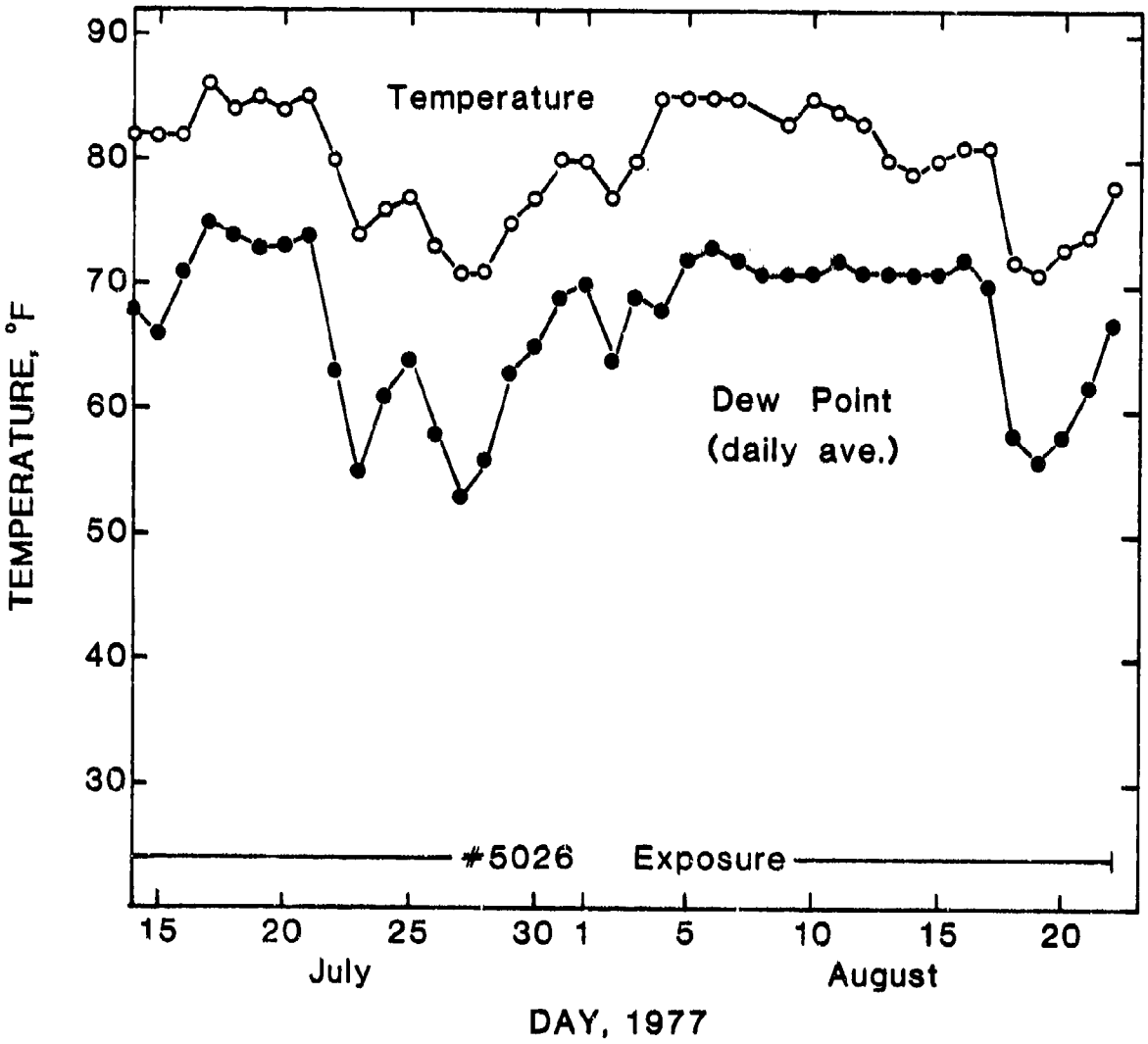

Figure 5. Variations of the Average Daily Temperature and Dew Point During Exposure 5026 at NRL

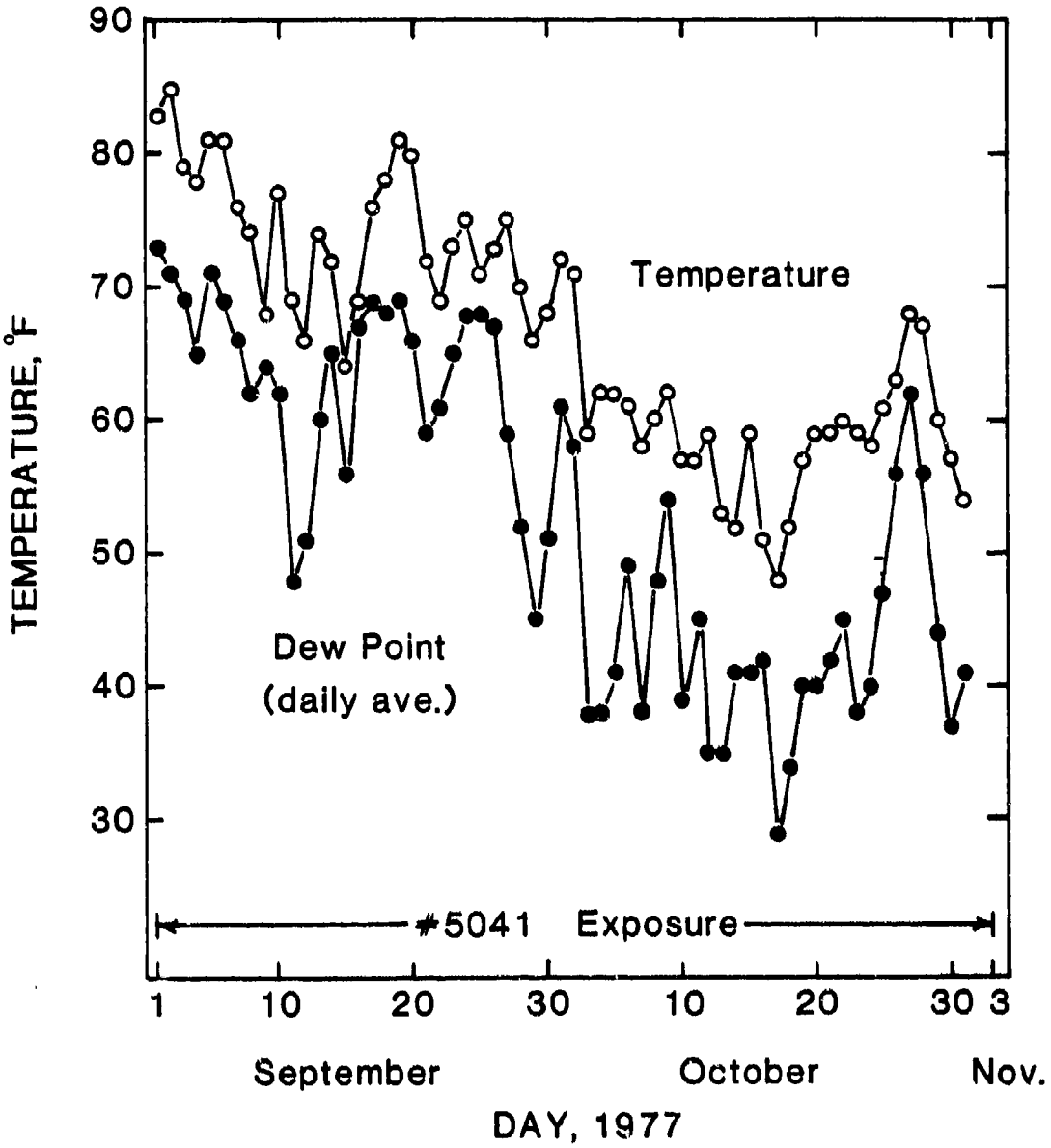

Figure 6. Variations of the Average Daily Temperature and Dew Point During Exposure 5041 at NRL

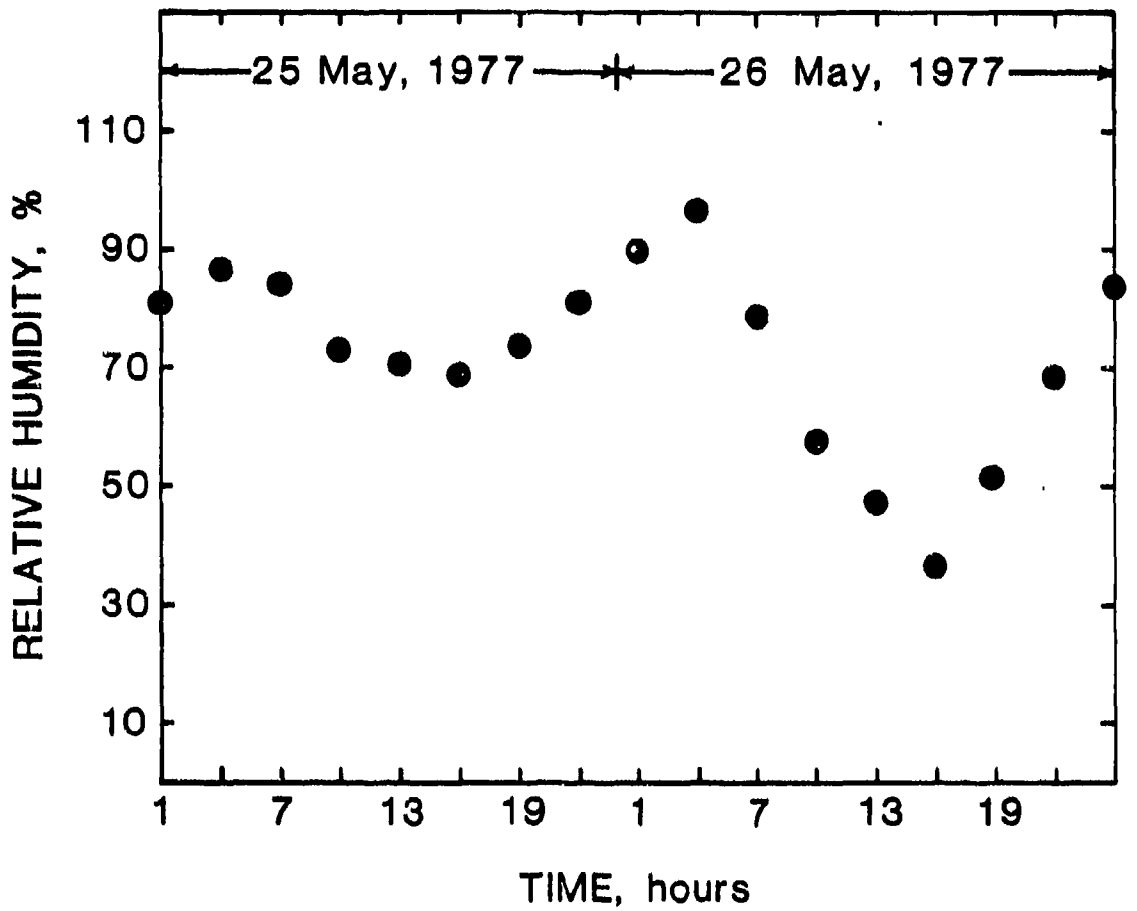

Figure 7. Example of Hourly Changes in Relative Humidity During Exposure 5011

TABLE 4. WEIGHT CHANGES OF WHETLERITE (LOT 2-281) AFTER EXPOSURES IN 1977

	Exposure	Layer, wt. change %			
		1	2	3	4
5011	3 May - 26 May	7.0	7.2	11.5	19.6
5018	2 Jun - 30 Jun	20.2	20.8	20.5	18.5
5026	14 Jul - 22 Aug	26.0	27.8	27.7	27.2
5041	11 Sep - 3 Nov	26.6	27.5	26.7	26.0
5062	16 Nov - 4 Feb 78	8.6	5.1	5.1	5.3

During the weathering in 1977, the values of the contaminants (ppm, V) that were present in the air were averaged over the exposure periods. These results, together with the duration and volumes of air, are summarized in Table 5.

TABLE 5. CONTAMINANTS (PPM) OBSERVED IN THE INLET AIR IN 1977 EXPOSURES

	Oxidants (O_3)	SO_2	NO_2	RHC	CO	Duration (days)	Air (M^3)
5011	0.015	0.020	0.047	0.22	0.32	23	1270
5018	0.020	0.020	0.116	1.06	0.98	28	2720
5026	0.04	0.023	0.078	0.07	0.95	39	4680
5041	0.015	0.015	0.075	0.06	1.15	53	7742
5062	0.013	0.025	0.055	0.41	1.53	81	10307

The breakthrough times (min) for CK using a 5g sample of each whetlerite are given in Table 6. It is apparent that the inlet layers of whetlerite suffer the greatest degradation and the remaining three layers are about equal.

TABLE 6. CK LIFE USING A 5g SAMPLE FOR EACH LAYER OF THE WEATHERED SAMPLES IN 1977 EXPOSURES

	CK Life (minutes)				
Layer	5011	5018	5026	5041	5062
1	19	20	7.3	11	11
2	23	-	16	21	30
3	25	-	18	26	33
4	26	34	16	27	36
control	64	67	56	48	50

C_o = 4 mg/L and breakthrough concentration = 8 μg/L

A good correlation is evident (Figure 8) between the CK life of the top layers and the summation of contaminants during the exposures (ozone, sulfur dioxide, and nitrogen dioxide). A corresponding attempt using the CK life for the 2nd, 3rd, and 4th layers showed no correlation. An equivalent correlation is to use the summation of CK removed by the top layer as the Y-coordinate (see Figure 9).

A further discussion of the influence of contaminants is given in Section 6, "Concluding Remarks".

Additional observations during the 1977 exposures were concerned with the distilled water extracts of the weathered whetlerites. The pH values of these extracts (Table 7) were significantly lower than the initial whetlerites (8.1-8.3). Moreover, the conditions during the winter months (Exposure 5062) yielded more acidic extracts than during the fall (Exposure 5041). Also, the water extracts of weathered samples were almost colorless compared to the yellow-orange appearance of new whetlerite.

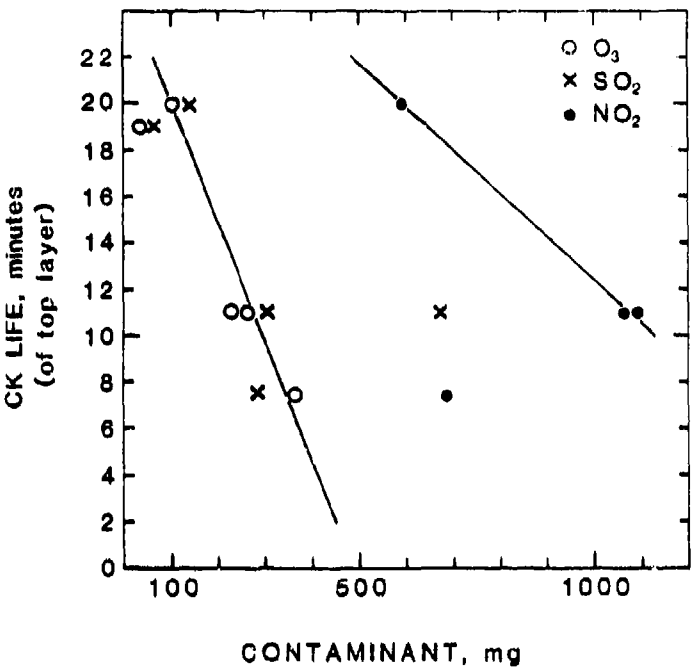

Figure 8. Correlation of CK Life of the Inlet Layer with the Summation of Contaminant Species (ozone, sulfur dioxide and nitrogen dioxide).

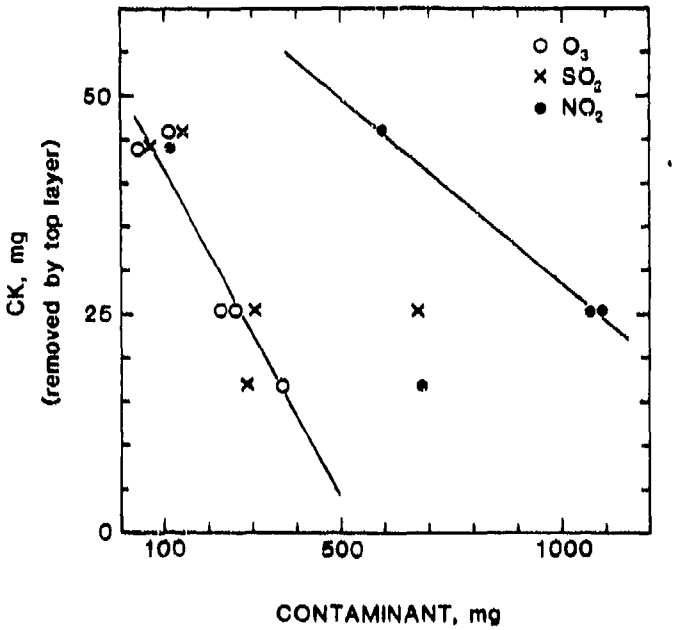

Figure 9. Correlation of CK Life of the Inlet Layer with the Summation of Contaminant Species; CK Expressed as mgs Removed by the Inlet Layer

TABLE 7. THE pH VALUES OF WATER EXTRACTS OF WEATHERED WHETLERITES

Exposure	pH Values			
	1st Layer	2nd layer	3rd layer	4th layer
5041 11 Sep to 3 Nov 77 (64 days)	6.1	6.5	6.9	7.0
5062 16 Nov 77 to 4 Feb 78 (81 days)	4.8	6.0	6.8	6.8

3. WEATHERING EXPERIMENTS IN 1979 – 1980

A total of the 25 exposures of whetlerite (Lot 2-281) in 1979-80 (Table 8) were at three locations for intervals up to 12 months: (1) Naval Research Laboratory in Building 207, (2) the Atmospheric Physics facilities of the Argonne National Laboratory, and (3) the Simi Valley Monitoring Station of the Air Pollution Control District of Ventura, Calif. The purpose of the twelve one-month exposures at NRL was to observe the seasonal variation over the entire year.

TABLE 8. SUMMARY OF EXPOSURES IN 1979-1980

NRL				Argonne, IL		Simi Valley, CA	
Test	Exposure months	Test	Exposure months	Test	Exposure months	Test	Exposure months
5155	12	5209	1	5160	12	5162	12
5159	7	5211	1	5161	4	5163	4
5168	3	5212	1	5193	8	5196	2.5
5177	1	5213	1	5194	2.5	5197	8
5186	1	5215	1	5203	5	5204	5
5200	1	5220	1				
5201	1	5225	1				
5202	1						

3.1 Monthly Exposures at NRL

A log of the 12-month exposures of whetlerite is given in Table 9. The average flow of outdoor air was 0.0996×10^6 cu.ft./month. The standard deviation of the twelve exposures, 0.00579, may be attributed mainly to the packing fluctuations

of whetlerite particles. With the bed cross-section of 0.0873 sq.ft., the average linear flow rate was 26 ft/min (7.9 m/min).

TABLE 9. WEATHERING OF WHETLERITE LOT 2-281: Monthly Variation, NRL (Jan 80-Jan 81)

No.	Period	Flow (ft^3)	pH				Wt Inc %
			1	2	3	4	
5177	11 Jan-11 Feb	0.101×10^6	5.65	6.46	6.80	7.02	3.30
5186	11 Feb-11 Mar	0.0956	5.70	6.70	6.92	7.20	3.01
5200	11 Mar-11 Apr	0.100	5.67	6.41	6.59	6.79	4.82
5201	11 Apr-9 May	0.0911	6.04	6.35	6.44	6.54	6.73
5202	9 May-11 Jun	0.1052	6.09	6.25	6.22	6.22	12.70
5209	11 Jun-17 Jul	0.1108	5.4	5.9	6.1	6.1	26.0
5211	17 Jul-15 Aug	0.0914	4.89	5.74	5.72	5.78	25.1
5212	15 Aug-16 Sep	0.1006	6.6	6.6	6.5	6.7	18.3
5213	16 Sep-17 Oct	0.0983	5.6	6.0	6.0	6.1	19.2
5215	17 Oct-18 Nov	0.1051	5.5	6.1	6.3	6.3	5.52
5220	20 Nov-22 Dec	0.1005	6.0	6.7	6.8	7.0	2.69
5225	22 Dec-22 Jan	0.0951	6.6	7.2	7.3	7.4	2.68

The monthly variation in weight-increase of the whetlerite samples exposed at NRL (Figure 10) follows closely the variation in the monthly average for dew points (Figure 1). Both show a maximum during July-August.

The pH of the water extracts of the inlet layer of whetlerite (see Table 9) becomes somewhat more acidic during July-August than for the other months of the year. This behavior too might be correlated in part with the dew point. The dew point by definition is directly proportional to the partial pressure of water vapor and the degradation reactions depend on

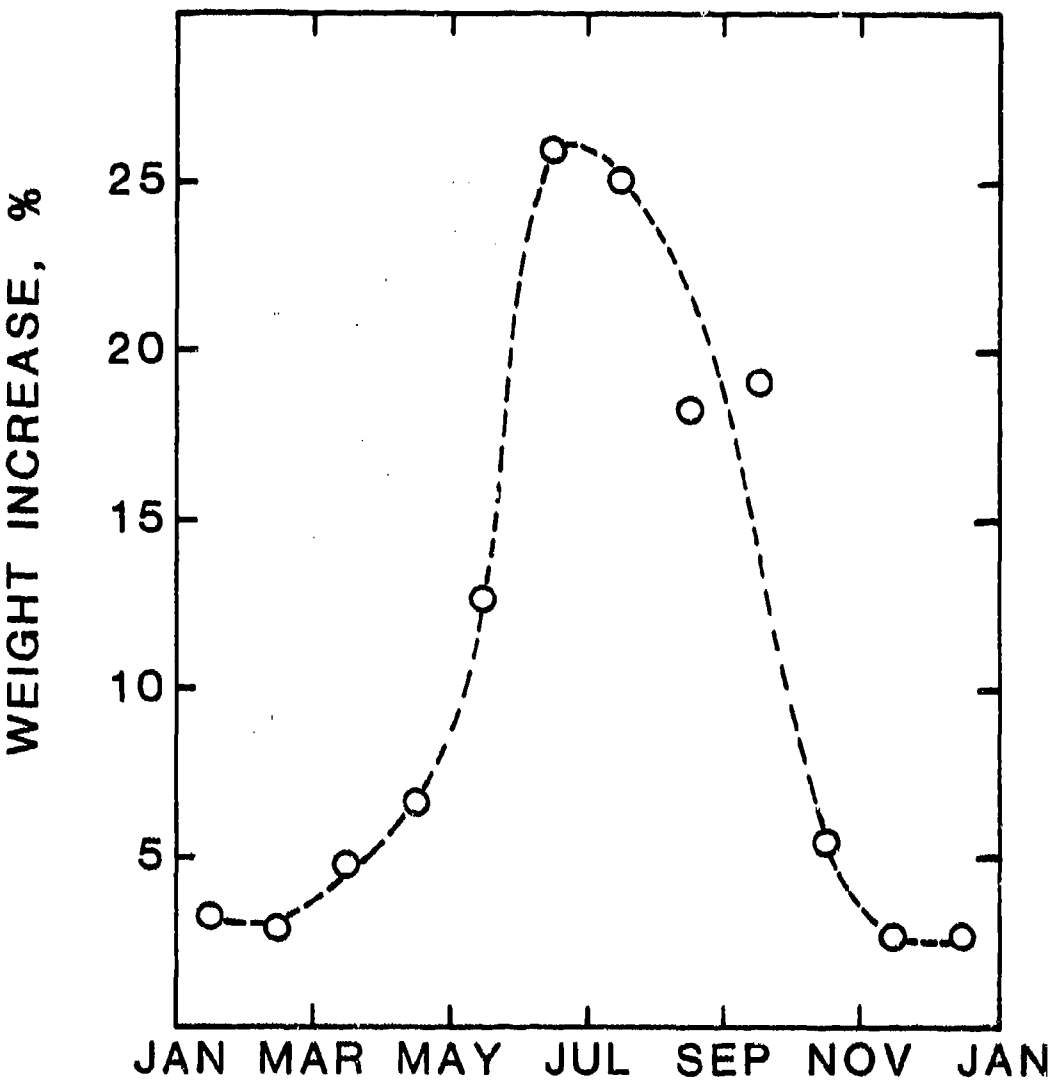

Figure 10. Monthly Variations in the Weight-Increase of Whetlerite Weathered at NRL in 1980

the activity of water vapor. The pH of the water extracts of the remaining three layers do not vary significantly; the average of the 36 values is 6.48, and the standard deviation is 0.45. Nevertheless, this value is significantly less than that of new whetlerite (pH of 8.1 to 8.3), and it is evident that the whetlerite particles in layers 2, 3, and 4 have also been subjected to some weathering modification. It has been shown by L. L. Pytlewski (2) that ASC carbon immersed under water (equal volumes of water and ASC carbon) showed no significant change in pH, remaining on the basic side at 8 to 8.5. The decrease in pH observed in weathering requires, therefore, the presence of oxygen and the other contaminants of the air in order to degrade the pH of whetlerite to the degree observed (Table 9).

3.2 Exposures for Periods Longer than One Month

The schedule in weathering whetlerite for periods greater than one month is given in Table 10. The average flow for all exposures was 0.0994×10^6 cu.ft. per month, with an average deviation of 0.0118×10^6. The performance of the Roton Blowers (SE2A-14) used in all of the installations was quite satisfactory. The variation in flow rates appears to be related to the fluctuations in packing the 4-inch diameter containers inasmuch as the same material (Lot 2-281) was used in all cases.

The dew point variability of outdoor air in the exposures at NRL was shown in Figure 1. It is evident that the yearly trends for 1977, 1978, 1979 and 1980 are similar and appear to be a general behavior of the climatological location of NRL.

The monthly averaged dew points are above 50°F for about half of the year, which is significant in regard to the adsorption of moisture by whetlerite. Over the year the dew points varied from 10° to 70°F, and from the partial pressure of water vapor, the water content varied from 4 to 40 g/m^3.

The summary of weathering whetlerite for periods greater than one month (Table 10) covers the three locations over a period of one year.

The yearly trends of dew point (monthly average) observed at the Chicago O'Hare Airport and at the Argonne National Laboratory are shown in Figure 11. The maximum also occurred in July and August, but the dropoff is steeper towards lower dew points in the earlier and later months. The carbons were exposed to air flows in the immediate neighborhood of air sampling at the Argonne National Laboratory, but there were only small differences when compared to the O'Hare Airport station. The averaging over the month hides local variations.

A similar situation was observed on comparing the recorded dew points at the Los Angeles International Airport with those calculated for Simi Valley from readings of the local temperatures and relative humidity. The annual trend of dew point (Figure 12) shows only a shallow maximum in July-August-September, and the total variation over the year was between 60° to 40°F. However, the daily averages may be subject to greater fluctuations, and thus influence the moisture content of the air flow through the whetlerite.

TABLE 10. WEATHERING OF WHETLERITE (Lot 2-281): PERIODS GREATER THAN ONE MONTH

	Exposure Period (months)						
	12	8	7	5	4	3	2.5
	Naval Research Laboratory						
Date	Jun 79 Jun 80		Sep 79 Apr 80			Nov 79 Feb 80	
Flow 10^6 cu.ft.	1.262		0.890			0.317	
Wt.incr. %	24.0		9.0			4.6	
	Argonne National Laboratory						
Date	Oct 79 Oct 80	Feb 80 Oct 80		May 80 Oct 80	Oct 79 Feb 80		Feb 80 May 80
Flow 10^6 cu.ft.	1.086	0.740		0.511	0.405		0.250
Wt.incr. %	28.6	28.4		28.7	26.9		28.8
	Simi Valley						
Date	Oct 79 Oct 80	Feb 80 Oct 80		May 80 Oct 80	Oct 79 Feb 80		Feb 80 May 80
Flow 10^6 cu.ft.	0.930	0.694		0.533	0.389		0.248
Wt. incr. %	12.6	12.4		6.45	27.8		21.3

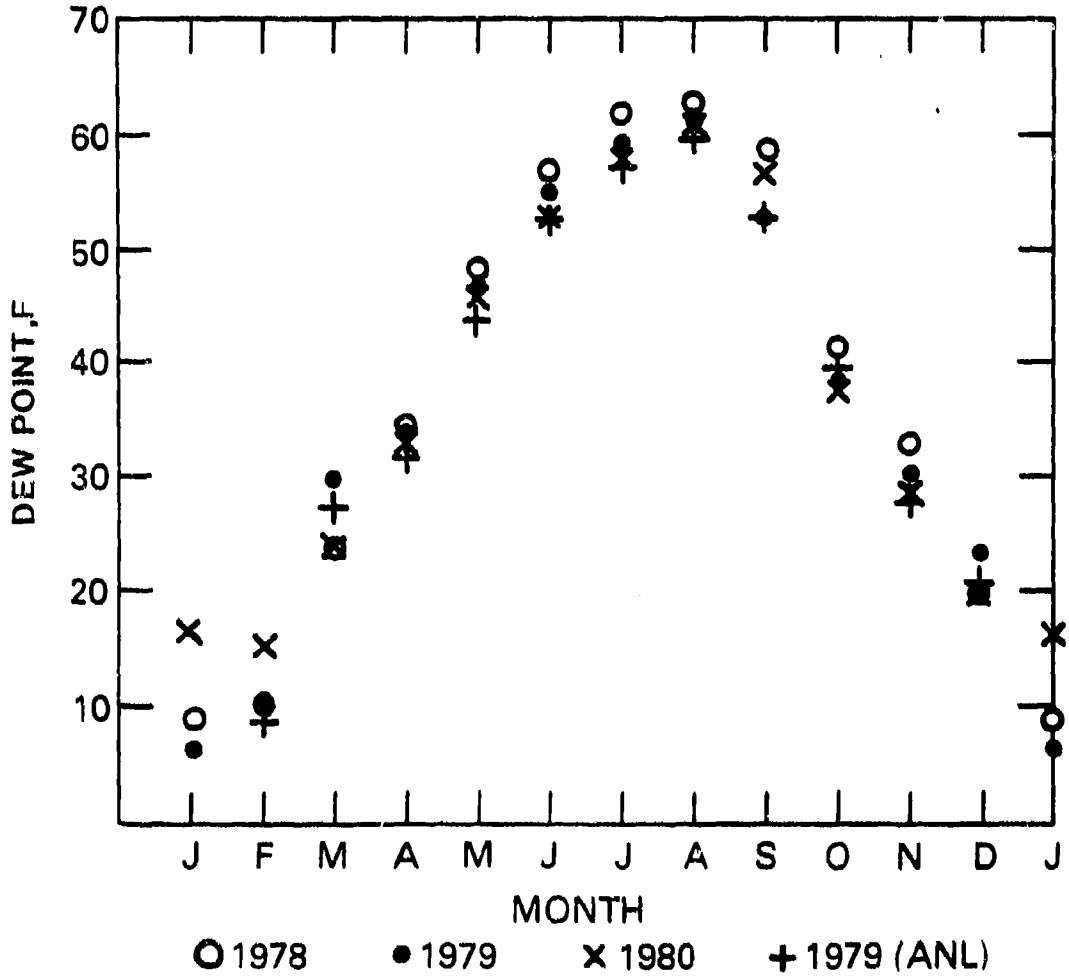

Figure 11. Monthly Averages of Dew Points Observed at Chicago O'Hare Airport and at the Argonne National Laboratory

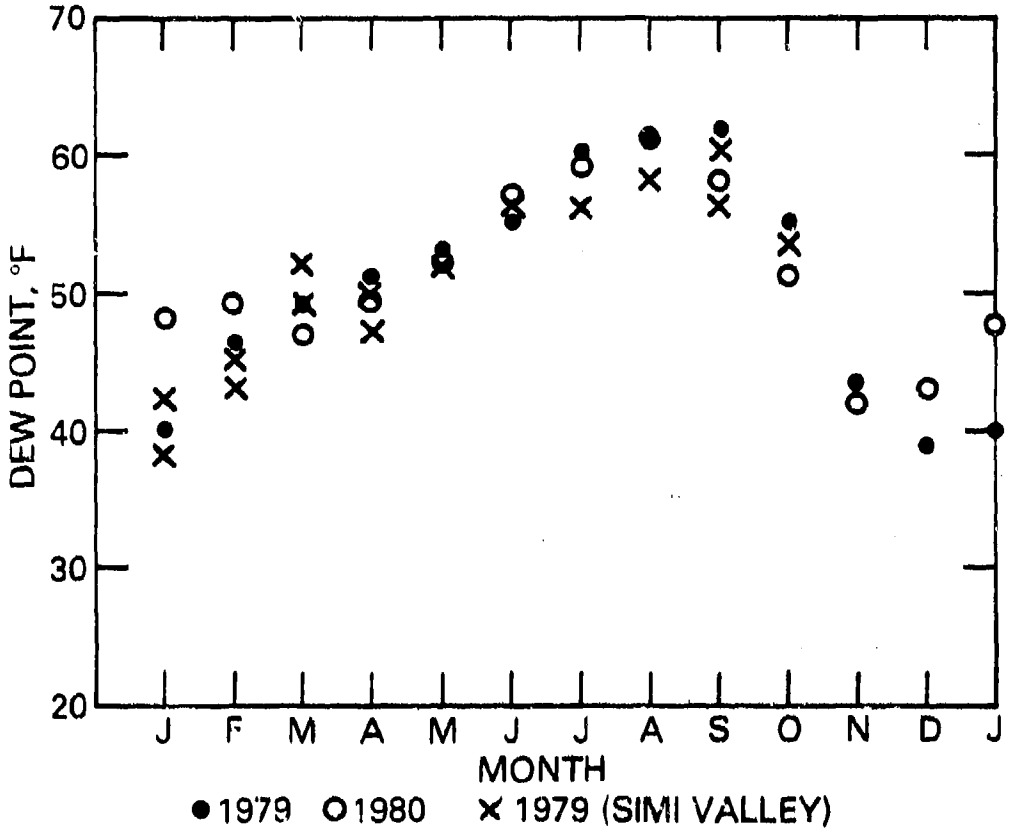

Figure 12. Monthly Average of Dew Points Observed at the Los Angeles International Airport and at Simi Valley, Ventura County, CA.

4. EVALUATION OF WEATHERED SAMPLES

4.1 Test Procedures

The weathered samples were evaluated with three test gases: (1) CK, cyanogen chloride, (2) DMMP, dimethylmethylphosphonate, and (3) AC, hydrogen cyanide. The test conditions are given below:

a. CK Tests:

(1) Equilibrated overnight with 75°F, 80% RH air.

(2) Charcoal weight: 5.0 g (dry weight).

(3) Relative humidity: 80%.

(4) Flow: 1.63 lpm (face velocity - 575 cm/sec).

(5) Challenge concentration: 4000 µg/liter.

(6) Breakpoint concentration: 8 µg/liter.

b. DMMP Tests:

(1) Charcoal weight 5.0 g (dry weight).

(2) Relative humidity: Ambient.

(3) Flow: 1.63 lpn,

(4) Challenge concentration: 4000 µg/l.

(5) Breakpoint concentration: 0.04 µg/l.

c. AC Tests:

(1) Charcoal weight: 5.0 g (dry weight).

(2) Relative humidity: 50%.

(3) Flow: 1.63 lpm.

(4) Challenge concentration: 10,000 µg/l.

(5) Breakpoint concentration: 7 µg/l.

4.2 Test Results

Control Data: CK Tests - 77.6 min ± 8.5
AC Tests - 23.2 min ± 0.5
DMMP Tests - 188.5 ± 13.5

4.21 NRL Samples

Sample	Dates of Use	Months in Use	% Change in wgt	Mean CK "life"	Mean DMMP "Life"	Mean AC "life"
5168-1	11/1/79 to	3	7.1	14.9	156	16.9
-2	2/1/80		4.1	57.9	182	20.6
-3			3.5	55.0	196	19.2
-4			3.8	55.2	186	20.1
5159-1	9/24/79 to	7	13.9	1.0	125	
-2	4/24/80		7.9	14.6	176	
-3			7.2	14.4	176	
-4			7.2	17.4	158	
5155-1	6/24/79 to	12	26.4	0.9	112	
-2	6/24/80		22.9	3.1	121	
-3			22.7	5.4	138	
-4			22.7	4.3	128	
5177-1	1/11/80 to	1	4.1	50.6	176	19.9
-2	2/11/80		2.9	69.2	192	20.9
-3			3.2	72.9	200	21.1
-4			3.1	75.4	202	22.4
5186-1	2/11/80 to	1	3.1	27.1	161	
-2	3/11/80		3.3	39.6	191	
-3			2.8	45.3	197	
-4			2.9	41.0	180	
5200-1	3/11/80 to	1	4.6	28.6	184	
-2	4/11/80		4.9	46.1	189	
-3			4.9	46.5	194	
-4			4.9	42.9	194	
5201-1	4/11/80 to	1	6.3	28.7	185	
-2	5/9/80		6.9	38.8	177	
-3			6.9	46.0	189	
-4			6.8	50.9	208	
5202-1	5/9/80 to	1	10.3	20.6		
-2	6/11/80		11.6	23.4		
-3			14.4	29.3		
-4			14.5	18.3		

(cont'd)

NRL Samples (Cont'd)

Sample	Dates of Use	Months in Use	% Change in Wgt	Mean CK "life"	Mean DMMP "life"	Mean AC "life"
5209-1	6/11/80 to	1	25.5	4.6	185	
-2	7/17/80		25.5	12.4	202	
-3			26.5	11.6	197	
-4			26.4	4.2	189	
5211-1	7/17/80 to	1	24.5	7.7	174	
-2	8/15/80		24.6	37.5	185	
-3			25.3	26.3	201	
-4			26.0	23.0	203	
5212-1	8/15/80 to	1	17.7		190	
-2	9/16/80		17.7	29.4	187	
-3			18.6	27.8	191	
-4			19.3	34.4	197	
5213-1	9/16/80 to	1	18.4	24.0	187	
-2	10/17/80		19.8	36.7		
-3			19.0	42.4	185	
-4			19.4	45.9	195	
5215-1	10/17/80 to	1	5.9	26.5	183	
-2	11/18/80		4.8	48.1	187	
-3			5.6	38.9	173	
-4			5.8	27.4	155	
5220-1	11/20/80 to	1	3.1	46.3	175	
-2	12/28/80		2.2	60.7	182	
-3			2.9	63.3	196	
-4			2.6	62.2	198	
5225-1	12/22/80 to	1	3.1	34.1	174	
-2	1/22/81		2.7	56.5	187	
-3			2.4	59.5	175	
-4			2.5	63.3	178	

4.22 Argonne Samples

5194-1	2/27/80 to	2.5	28.6	2.9	176	
-2	5/13/80		28.7	13.9	177	
-3			27.9	13.2	172	
-4			30.0	6.6	161	
5161-1	10/22/79 to	4	27.1	9.0	187	
-2	2/24/80		27.1	36.7	183	
-3			27.0	37.8	176	
-4			26.6	36.7	187	

(cont'd)

Argonne Samples (Cont'd)

Sample	Dates of Use	Months in Use	% Change in Wgt	Mean CK "life"	Mean DMMP "life"	Mean AC "life"
5203-1	5/13/80 to	5	26.7	2.8		
-2	10/20/80		29.4	12.4		
-3			29.5	19.1		
-4			29.1	25.1		
5193-1	2/27/80 to	8	27.3	2.5	195	
-2	10/24/80		28.1	11.9	214	
-3			28.6	15.2	166	
-4			29.4	22.6	200	
5160-1	10/22/79 to	12	29.3	1.2	204	
-2	10/28/80		28.8	10.3	190	
-3			28.5	10.4	178	
-4			27.8	16.3	187	
4.23	Simi Valley Samples					
5196-1	2/28/80 to	2.5	16.3	6.8	181	
-2	5/14/80		21.4	48.0	176	
-3			22.6	46.7	181	
-4			24.9	44.7	182	
5163-1	10/24/79 to	4	25.4	5.2	171	
-2	2/28/80		28.5	14.4	189	
-3			28.1	12.1	172	
5204-1	5/14/80 to	5	9.1	1.4		
-2	10/24/80		5.4	12.6		
-3			5.6	11.8		
-4			5.7	8.2		
5197-1	2/28/80 to	8	8.8	1.1	181	
-2	10/24/80		12.4	10.9	191	
-3			14.0	21.5	197	
-4			14.5	17.4	192	
5160-1	10/24/79 to	12	11.1	0.8	180	
-2	10/24/80		13.5	4.6	183	
-3			13.5	4.9	164	
-4			12.1	-	199	

4.3 Influence of Time, Season, and Location

In view of the seasonal change in dew point (Figure 1), a correlation was sought among the samples weathered monthly at NRL. The influence on CK life of these samples is shown in Figure 13. The lower points (in circles) are for whetlerite removed from the entrance layer, and the upper points (x) are for whetlerite removed from the exit layer; the gradient through the two-inch sample bed is evident. There is an inverse relationship between Figures 1 and 13 which demonstrates that the

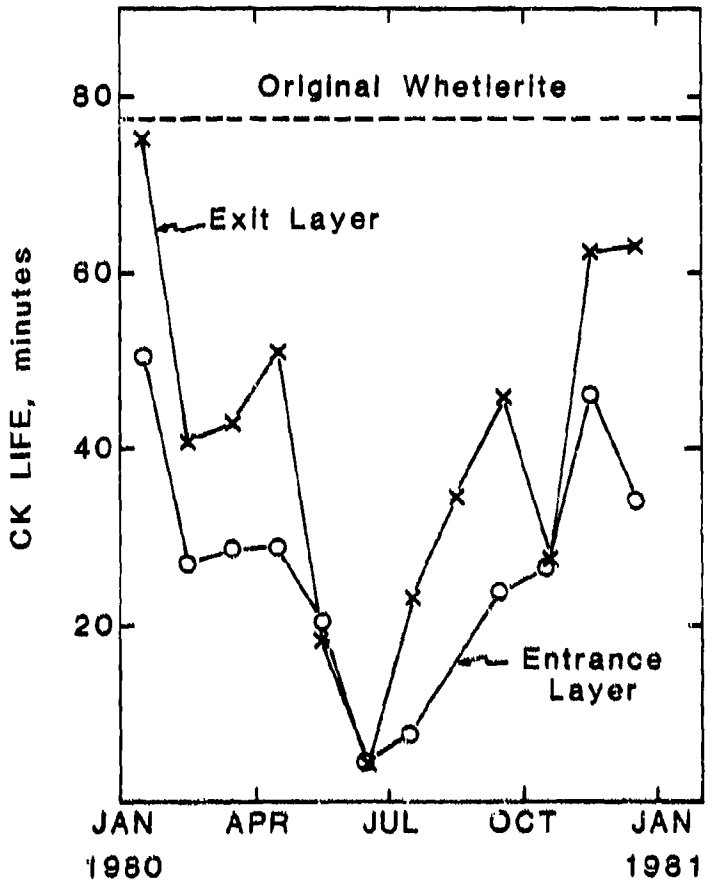

Figure 13. Influence on CK Life after Weathering Whetlerite (2-281) in One-Month Intervals at NRL

water content of the air is one of the important parameters in the degradation of the CK activity.

In contrast to CK behavior, the DMMP activity was not adversely affected by seasonal variation. The 43 measurements of the one-month exposures at NRL gave a mean life of 187 minutes with a standard deviation of 11; the control for non-weathered samples was 188.5 minutes.

Comparisons are made (Table 11) for the performance of weathered whetlerites against CK and DMMP relative to the control values. There is a steady degradation with time as well as with the depth of the weathered sample. All new samples of whetlerite show a simple exponential attenuation of activity with depth, but for weathered carbons, the depth profile is quite unpredictable. The greatest penetration of CK (Table 11) is through the inlet layer of each sample and the penetrations through each of the remaining three layers tend to a constant value. However, it is important to note that the penetration in all cases is considerably more than for original whetlerite. This behavior is compatible with a nonuniformity in the degradation reactions of the contaminants responsible for weathering. For example, the depth profile for exposures of short duration indicate a fairly constant penetration in layers 2, 3 and 4. The depth profile is less uniform for exposures of long duration.

The results for DMMP are location-dependent. The DMMP life at the Argonne and Simi Valley locations was not adversely affected after 12-month exposures, but those at NRL showed a

TABLE 11. FRACTIONAL PERFORMANCE OF WEATHERED WHETLERITE (5 g dry wt) COMPARED TO NEW WHETLERITE

Sample	Months	Exposure Dates	Weathered Layer 1	2	3	4
		NRL				
5168	3	CK 1 Nov 79 to	0.192	0.668	0.709	0.711
		DMMP 1 Feb 80	0.828	0.966	1.04	0.987
5159	7	CK 24 Sep 79 to	0.013	0.188	0.186	0.224
		DMMP 24 Apr 80	0.663	0.934	0.934	0.838
5155	12	CK 24 Jun 79 to	0.012	0.040	0.070	0.055
		24 Jun 80	0.594	0.642	0.732	0.679
		Argonne				
5194	2.5	CK 27 Feb 80 to	0.037	0.179	0.170	0.085
		DMMP 13 May 80	0.934	0.939	0.912	0.854
5161	4	CK 22 Oct 79 to	0.116	0.473	0.487	0.473
		DMMP 27 Feb 80	0.992	0.971	0.934	0.992
5203	5	CK 13 May to	0.036	0.160	0.246	0.323
		DMMP 20 Oct 80				
5193	8	CK 27 Feb to	0.032	0.153	0.196	0.291
		DMMP 20 Oct 80	1.03	1.13	0.881	1.06
5160	12	CK 22 Oct 79 to	0.015	0.133	0.134	0.210
		DMMP 20 Oct 80	1.08	1.01	0.944	0.992
		Simi Valley				
5196	2.5	CK 28 Feb 80 to	0.088	0.619	0.602	0.576
		DMMP 14 May 80	0.960	0.934	0.960	0.966
5163	4	CK 24 Oct 79 to	0.067	0.186	0.156	0.156
		DMMP 28 Feb 80	0.907	1.00	0.912	0.944
5204	5	CK 14 May 80 to	0.018	0.162	0.152	0.106
		DMMP 24 Oct 80				
5197	8	CK 28 Feb 80 to	0.014	0.140	0.277	0.224
		DMMP 24 Oct 80	0.960	1.01	1.04	1.01
5162	12	CK 24 Oct 79 to	0.010	0.059	0.062	
		DMMP 24 Oct 80	0.954	0.971	0.870	1.05

Note: First result for each sample is CK and the second result is DMMP.

reduction of 30 to 40% after the 12-month exposure. An explanation may reside in the individual contaminants in the air at the three locations.

The changes in pH of the water extracts for exposures longer than one month (Table 12) are more uniform at the three locations. The trend in all cases is to low pH with duration of weathering. As discussed above, the drop in pH from the initial value 8.1 to 8.3 is already detected in one-month exposures (pH 6 to 7) and after one year, a pH of 4.1 was observed. The change is obviously significant since it corresponds to a decrease from 10^{-8} to 10^{-4} in H^+ activity.

TABLE 12. CHANGES IN pH FOR EXPOSURES LONGER THAN ONE MONTH

Months	NRL				Argonne				Simi Valley			
	1	2	3	4	1	2	3	4	1	2	3	4
2.5					5.9	6.1	6.2	6.3	5.7	6.0	6.1	6.2
3	4.6	5.9	6.0	6.0								
4					4.9	5.9	5.9	5.9	5.4	5.8	5.8	5.9
5					5.1	5.8	6.0	6.0	4.3	5.4	5.6	5.7
7	4.2	5.7	5.9	6.1								
8					4.5	5.7	5.8	5.8	4.4	5.2	5.2	5.4
12	4.1	5.2	5.9	6.0	4.1	5.8	5.7	5.8	4.5	5.4	5.5	5.6

4.4 Influence of the Contaminants of the Air

The environmental contaminants reported by many EPA investigators include the four ubiquitous gaseous pollutants - ozone, sulfur dioxide, nitric oxide, and nitrogen dioxide. These are subject to daily, seasonal, and annual variations. Other

contaminants, including carbon monoxide, methane, and other volatile hydrocarbons, do not seem to influence the weathering of whetlerite. The charcoal-exposure studies at NRL have made use of the available results from the NRL Air Quality Monitoring Station (Code 6072) (4).

The total of each contaminant introduced in the air flow through the sample during the monthly exposures was calculated for O_3, SO_2, NO, and NO_2. The results (Table 13) are expressed as the weight (g) of each species contained in the measured volume of air. In a previous section, a correlation was indicated between the CK life of weathered whetlerite and the moisture content of the air (Figure 13). It is now necessary to explore the additional role of the contaminants in the degradation process. The observed CK life behavior, of course, results from the superposition of all contaminants that have reacted with the whetlerite.

The graphs in Figure 14 illustrate the seasonal distribution of the four contaminants at NRL. The inverse behavior of ozone and sulfur dioxide is evident and the levels of nitric oxide and nitrogen dioxide are approximately constant. Using the weights of contaminants in Table 13, the mean of nitric oxide is 0.071 with a standard deviation of 0.036; the mean of nitrogen dioxide is 0.15 with a standard deviation of 0.03.

The relative effect of each contaminant in reducing the CK life of whetlerite is not known. Previous experimental studies with other adsorbent carbons suggest a high degradation in each case at the contaminant levels involved. With this

TABLE 13. TOTAL CONTAMINANT INTRODUCED DURING THE MONTHLY EXPOSURES IN 1980 AT NRL (220g WHETLERITE, Lot 2-218)

NRL Test	Air Vol. 10^6c.f.	Ozone		SO_2		NO		NO_2	
		ppm	wt.g	ppm	wt.g	ppm	wt g	ppm	wt g
5177	.101	.013	.080	.030	.25	.035	.13	.020	.21
5186	.0956	.016	.093	.030	.23	.034	.12	.023	.19
5200	.100	.030	.18	.034	.28	.017	.064	.018	.10
5201	.0911	.033	.18	.026	.19	.014	.048	.021	.11
5202	.1052	.037	.24	.019	.16	.016	.064	.023	.14
5209	.1108	.030	.20	.018	.16	.009	.038	.023	.15
5211	.0914	.041	.23	.018	.13	.009	.031	.03o	.16
5212	.1006	.045	.28	.016	.13	.005	.019	.020	.12
5213	.0983	.035	.21	.013	.10	.013	.048	.023	.13
5215	.1051	.021	.13	.014	.12	.023	.092	.029	.18
5220	.1005	.024	.15	.016	.13	.026	.099	.022	.13
5225	.0951	.008	.046	.039	.30	.028	.101	.024	.13

assumption for whetlerite, the summations of the four contaminants may be seen (Figure 15) to be approximately constant over the twelve monthly exposures in 1980.

As a result, the observed CK life of whetlerite in 1980 was subjected to a constant influence from the integrated four contaminants and, therefore, the suggested correlation with a variable water content may have merit. The synergistic effect of water vapor and the contaminants, ozone, sulfur dioxide, nitric oxide, or nitrogen dioxide, cannot be neglected.

One consequence of the weathering reaction is a reduction of the chromate content observed in the water extract. The

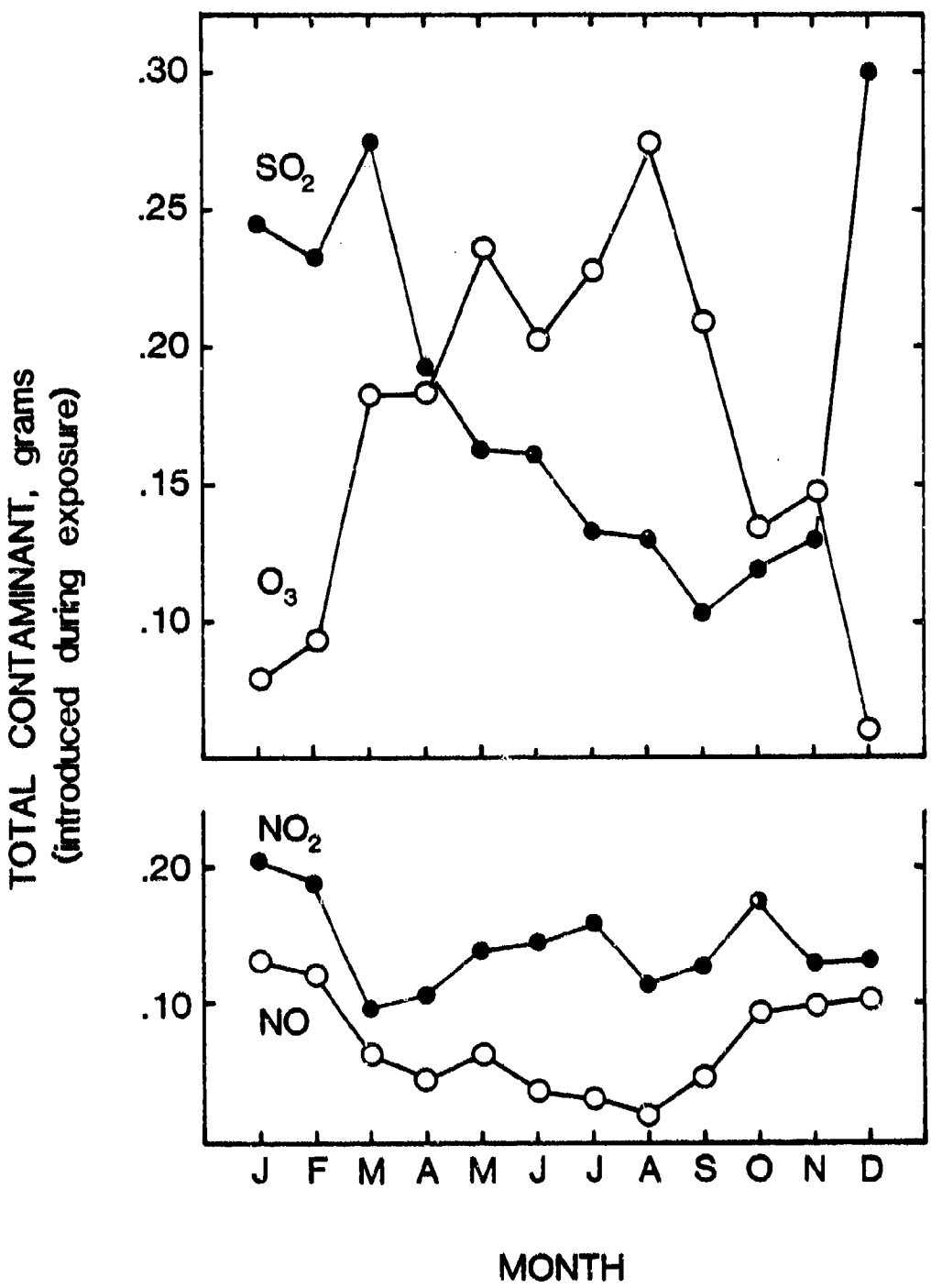

Figure 14. The Seasonal Distribution of Four Contaminants in the Inlet Air at NRL

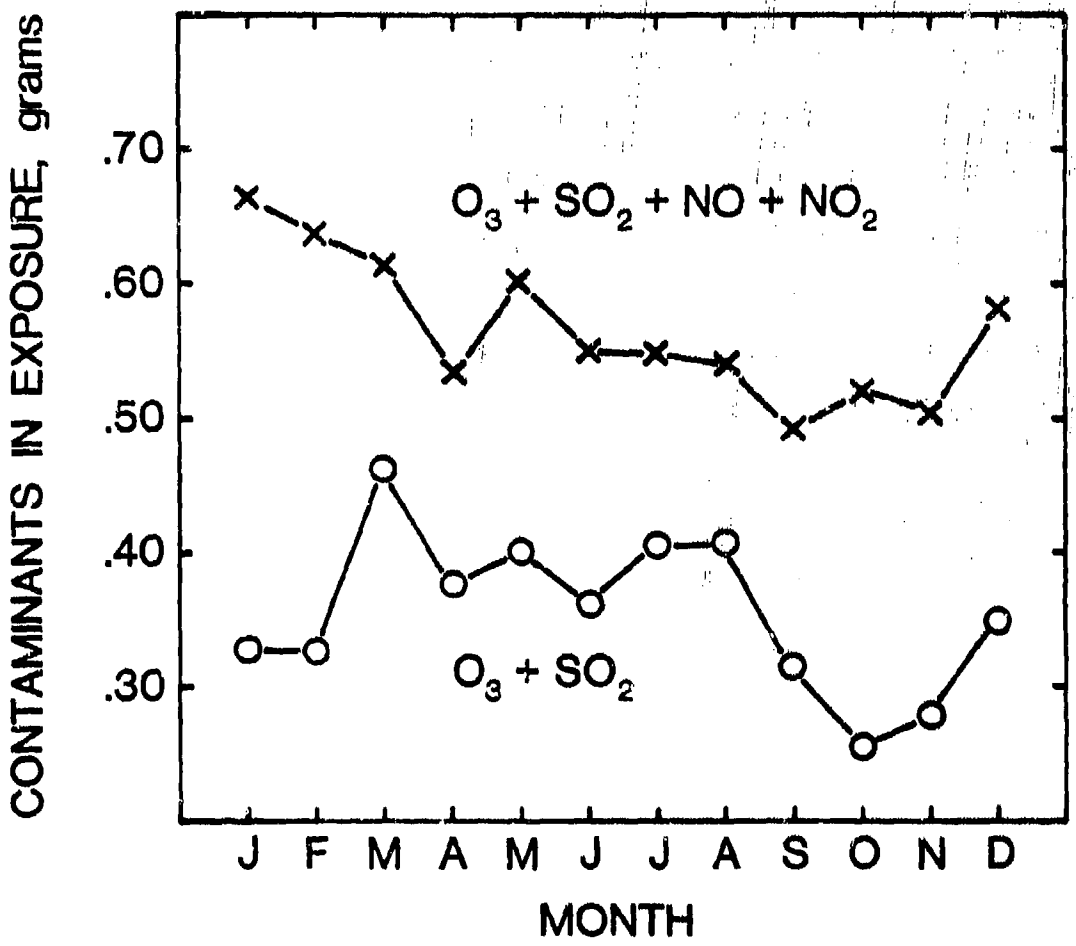

Figure 15. Summation of Four Contaminants in the Inlet Air during Monthly Exposures at NRL, 1980

chromium content of the original ASC impregnating solution is about four wt.percent. Only a small fraction of this was found to be desorbed into the water extracts mentioned previously in the determination of the pH (Table 12). The chromate concentration was determined from the spectrophotometric absorption at 375 nm. The average value for the extracts of new whetlerite (Lot 2-281) was 650 µg/ml. The chromium concentrations in the water extracts of three weathered whetlerites are plotted in Figure 16 as a function of depth (layer 1 signifying the inlet layer) and the duration of the exposures. After one year the water extract contained only 1% of the chromium observed in new whetlerite. After three months, a strong gradient in extractable chromate was already observed in the depth profile of the whetlerite. Recent observations have located a second absorption peak at 275 nm in the water extracts. These are in the same sequence of absorptivity as those observed at 375 nm and have not as yet been interpreted.

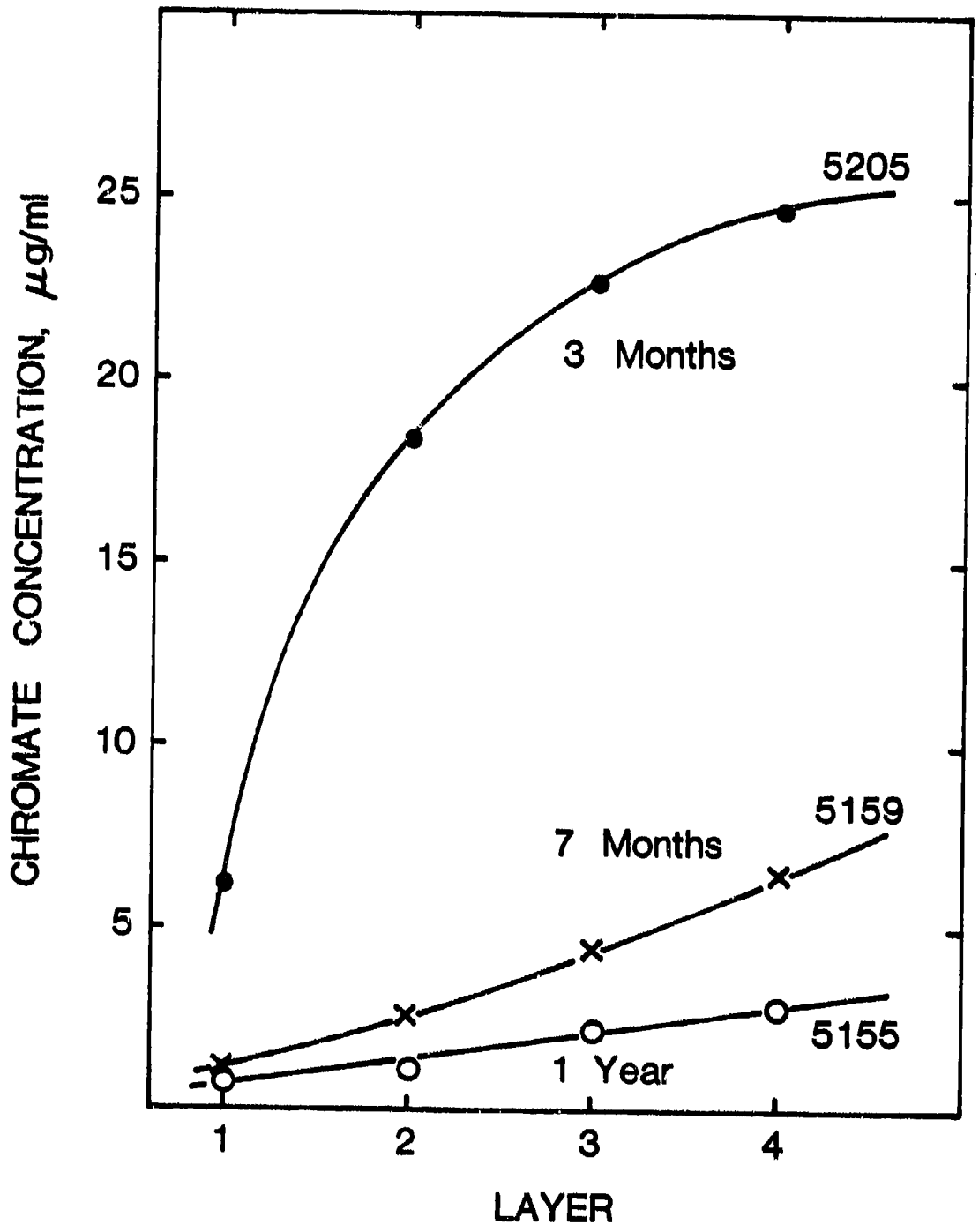

Figure 16. The Chromate Concentrations in the Water Extracts of Weathered Whetlerites as a Function of Depth Profile and Duration of the Exposure.

5. CONCLUDING REMARKS

The CK "life" of whetlerite is essentially destroyed as the result of the exposure to outdoor air during the hot and humid summer months or in warm climates. Whetlerite is relatively stable in outdoor air flows during cool, dry winter months.

The results for DMMP are location-dependent. The DMMP life at the Argonne and Simi Valley locations was not adversely affected after twelve-month exposures, but those at NRL showed a reduction of 30 to 40% after the twelve-month exposure. An explanation may reside in the individual contaminants in the air at the three locations.

The greatest penetration of CK is through the inlet layer of each sample and the penetration through each of the remaining three layers tends to be constant. However, the penetration in all cases is considerably more than for an original whetlerite. This behavior is compatible with a nonuniformity in the degradation reactions of water vapor plus contaminants during the weathering.

A good correlation was found between the loss of CK activity and the dew point of the air flow.

Since the loss of CK activity is accompanied by a loss in water-extracted chromate, it might be necessary in any regeneration system to effect an oxidation from Cr^{+3} to Cr^{+6}. A water-soluble reaction has been found to do this *in vitro*. It has yet to be accomplished *in carbono*.

6. REFERENCES

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APPENDIX 1 — LIST OF FIGURES

APPENDIX 2 — LIST OF TABLES